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Thermal and Hydrolytic Stabilities
of
(4-Carboranylbutyl) Methylsiloxane-
Dimethylsiloxane Copolymers

SR 007-03-03, Task 1000

Lab. Project 9400-31, Technical Memorandum 8

10 MAY 1965

TECHNICAL MEMORANDUM

U.S. NAVAL APPLIED SCIENCE LABORATORY
NAVAL BASE
BROOKLYN, NEW YORK 11251

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Physical Sciences Division

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Ref: (a) NAVAPLSCIENLAB Program Summary dated 1 Nov 1964, SR 007-03-03, Task 1000

(b) NAVAPLSCIENLAB Lab. Project 9400-31 Technical Memorandum 2 of 31 Jan 1964.

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1. TGA Thermogram of Carborane Silicone Elastomer Gum.
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3. Differential TGA Thermogram of Carborane Silicone Elastomer Gum.
4. Differential TGA Thermogram of Copolymer E107-5309 (RM)
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6. ITGA Thermogram of Copolymer E107-5309 (RM) at 300°C.
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8. ITGA Thermogram of Copolymer E107-5309 (RM) at 500°C.
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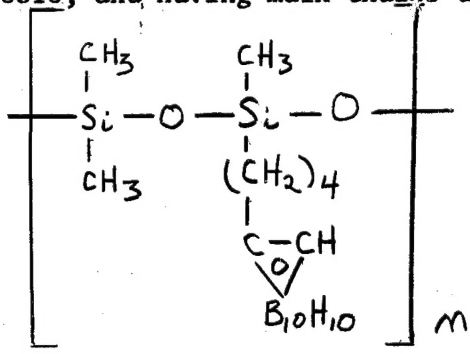
13. Infrared Spectra of (A) Untreated Carborone Silicone Elastomer Gum; (B) After 4 Hrs. In Boiling H_2O; and (C) After 24 Hrs. In H_2O at Room Temperature.
14. Infrared Spectra of (A) Untreated Copolymer E107-5309 (RM); (B) After 4 Hrs. In Boiling H_2O; and (C) After 24 Hrs. In H_2O at Room Temperature.

Table: 1 - Results of Thermogravimetric Analysis (TGA)

1. Under the High Temperature Polymer Program authorized by reference (a), the Naval Applied Science Laboratory is investigating the potential suitability of new polymeric materials developed by other research laboratories under government sponsorship for Naval use at elevated temperatures.

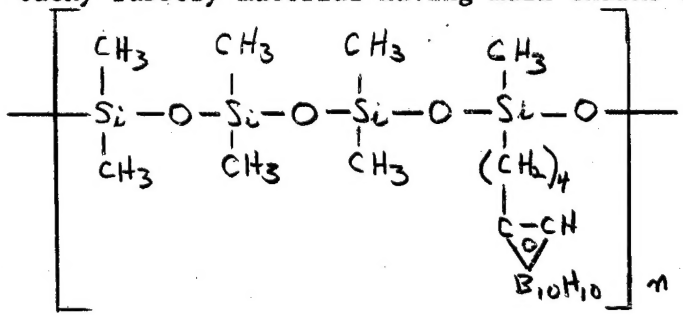
2. Work was conducted by A.A. Stein under the supervision of B.B. Simms, Organic Chemistry Branch Head. The Bureau of Ships Program Manager is E.A. Bukzin Code 342A and the Project Engineer is W.B. Shetterly, Code 634C4.

3. Reference (b) reported the results of studies made of the thermal resistance of a tough, flexible solid experimental polymer developed by the Reaction Motors Division of Thiokol Chemical Corp. under Bureau of Ships Contracts NObs 84774 and 88318, and having main-chains as follows:



(I)

In continuation of this work, there are reported herein the results of investigations of the thermal resistance and hydrolytic stability of two high molecular weight (4-carboranylbutyl) methylsiloxane-dimethylsiloxane coplymers designated by Reaction Motors as "carborane silicone elastomer gum", a soft, brown, slightly tacky rubbery material having main-chains as follows:



(II)

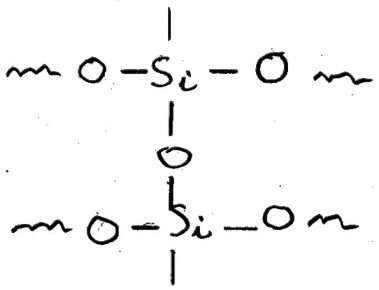
and "carborane silicone copolymer E 107-5309 (RM)", a clear, stiff, very slightly tacky, somewhat brittle, gummy substance having repeating units shown in I, above.

4. The thermal stabilities of the copolymers were investigated by thermogravimetric analyses (TGA). Essentially, this involved heating 0.20 gram samples at 180°C./ hr. in air. The results of these studies are shown in Table 1 and Figures 2 and 3. In general, these data indicate that copolymer E 107-5309 (RM) is more heat resistant than is the elastomer gum; attributable probably to the stabilizing influence of the 4-carboranylbutyl group which is present in greater number in the former product. The differential TGA thermograms shown in Figures 4 and 5 indicate that the weight loss of substance E 107-5309 (RM) attains maximum rates of 5.49 mg./min. at about 485°C and 505°C, respectively, where the elastomer gum pyrolysis products volatilize most rapidly at a rate of 1.62 mg./min. at approximately 405°C. In addition, the TGA and differntial TGA thermograms of product E 107-5309 (RM) closely resemble those shown by the lower molecular weight copolymer reported previously under reference (b). This indicates the degree of attack of these polymers is not influenced by the number of repeating chain units and suggests, therefore, that the thermal degradation proceeds by a random mechanism.

5. The potential suitablity of the polymers for use at elevated temperatures over extended time intervals in the presence of air was investigated by isothermal thermogravimetric analysis (ITGA) at 300 and 500°C. In this case, about 0.20 gram samples were inserted into a furnace that was previously heated to the desired temperature and weight changes were measured over approximately 6 hrs. These data are presented in figures 6 through 9. At 300°C., the elastomer gum shows a weight loss of 2.8% after 10 min., the weight then increased by about 0.2% during the next 30 min., decreased to a maximum loss of 3.5% at the end of 2 hrs.; thereafter the product gained weight at an average rate of 1.5×10^{-2} mg./min. At the end of 6 hours exposure the total weight loss was 1.8%; the surface of the sample was darkened, hardened, and embrittled while the remainder of the material appeared to be unaffected. Oxidative deterioration of the entire sample was apparently inhibited by the protecive barrier created by the degraded polymeric surface of the test specimen. Under the same test condition, copolymer E 107-5309 (RM) showed a weight loss of 1.5% after 10 min. exposure to 300°C., and then, unlike the elastomer gum, this material continued to lose weight at an average rate of approximately 3.5×10^{-2} mg./min. After 6 hrs., the weight loss was 7.8% and the residue had darkened to a light amber color, was slightly stiffened, but otherwise unaffected. At 500°C., the elastomer gum exhibited a 55.9% weight loss after 10 min. and then gained weight very slightly, at an average rate of 2.4×10^{-3} mg./min. After 6 hrs. exposure, the total weight loss was 55.6% and the residue appeared to be a grey to black, hard, brittle powder. When similarly treated, copolymer E 107-53 (RM) ignited and burned vigorously. This material showed weight loss of 68.0% and 79.4% after 10 and 20 minutes exposure, respectively. Thereafter, it continued to lose weight very slowly, at an

average rate of 4.4×10^{-4} mg./min. After 6 hours exposure, after its total weight loss was 79.5%, the residue was a tan, hard, brittle powder.

6. The infrared spectra of the original polymers and their residues after ITGA studies are shown in Figures 10 through 13. The spectra of the unheated polymers were obtained by attenuated total reflectance techniques while the spectra of the ITGA residues were made from Nujol mulls. After 6 hrs. at 300 and 500°C., the spectra of the elastomer gum and copolymer E 107-5309 (RM) residues show an absorption band at 3.12u, characteristic of Si-OH bonding, which does not appear in the spectra made from the unheated products. The Si-CH_3 linkages in the untreated polymers is well-marked in their spectra by an absorption made at 7.98u. In the spectra made from the residues obtained after heating the polymers for 6 hrs. at 300°C. the intensity of this absorption frequency appears to have appreciably decreased. After similar exposure at 500°C., the 7.98u band is not present in the elastomer gum residue spectrum and only appears as a very weak absorption in the spectrum shown by the residue from copolymer E 107-5309 (RM), after 6 hrs. at 500°C. These spectral changes suggest that during the heating process Si-CH_3 linkages are cleaved to probably give active Si - sites which can interact in the presence of oxygen to form crosslinks between chains of the type:



Main-chain cleavage of Si-O bonds is also possible. The active $\geqslant$Si - or $=$Si - O - sites thus formed would then interact with H_2O, formed possibly by oxidation of CH_3 groups, to give Si - OH linkages. The frequencies at 3.90 and 13.87u assignable in the original polymer spectra to B-H and - $(CH_2)_4$ - linkages, respectively, which are attributed to the 4-carboranylbutyl units seem to be only slightly changed in the spectra given by the 300°C. treated polymers and appear as weaker modes in the spectra obtained from the 500°C. residues. The presence of these frequencies and the decrease or absence of the absorption band at 7.98u in the residues produced by the 300 and 500°C. treatments indicate the superior thermal stability of the 4-carboranylbutyl group over that of the CH_3 unit. In addition, the weak 7.98u absorption frequency shown in the spectrum of the 500°C. residue from copolymer E 107-5309 (RM) as compared to its complete disappearance in the spectrum from the elastomer gum residue at 500°C. suggests that the 4-carboranylbutyl group might be stabilizing the polymer against the thermal and oxidative attack of CH_3 groups attached to the same Si atom.

7. The resistance of the polymers to immersion in boiling water and in water at room temperature for 4 and 24 hours, respectively, was investigated. Infra-

red spectra before and after the water immersion tests are shown in Figures 14 These data, together with visual examination before and after the immersion tests, indicate that these polymeric products are unaffected by exposure to water under the experimental conditions decribed herein.

8. It is concluded that the copolymers under study are potentially useful for the fabrication of elastomeric products intended for use at 300°C. over extended time intervals. For shorter time periods, the elastomer gum and copolymer E 107-5309 (RM) are probably suitable for use up to temperatures of about 350 and 400°C., respectively. The products exhibit excellent resistance to hydrolytic attack.

A. D. Delman

A. D. DELMAN
Principal Investigator

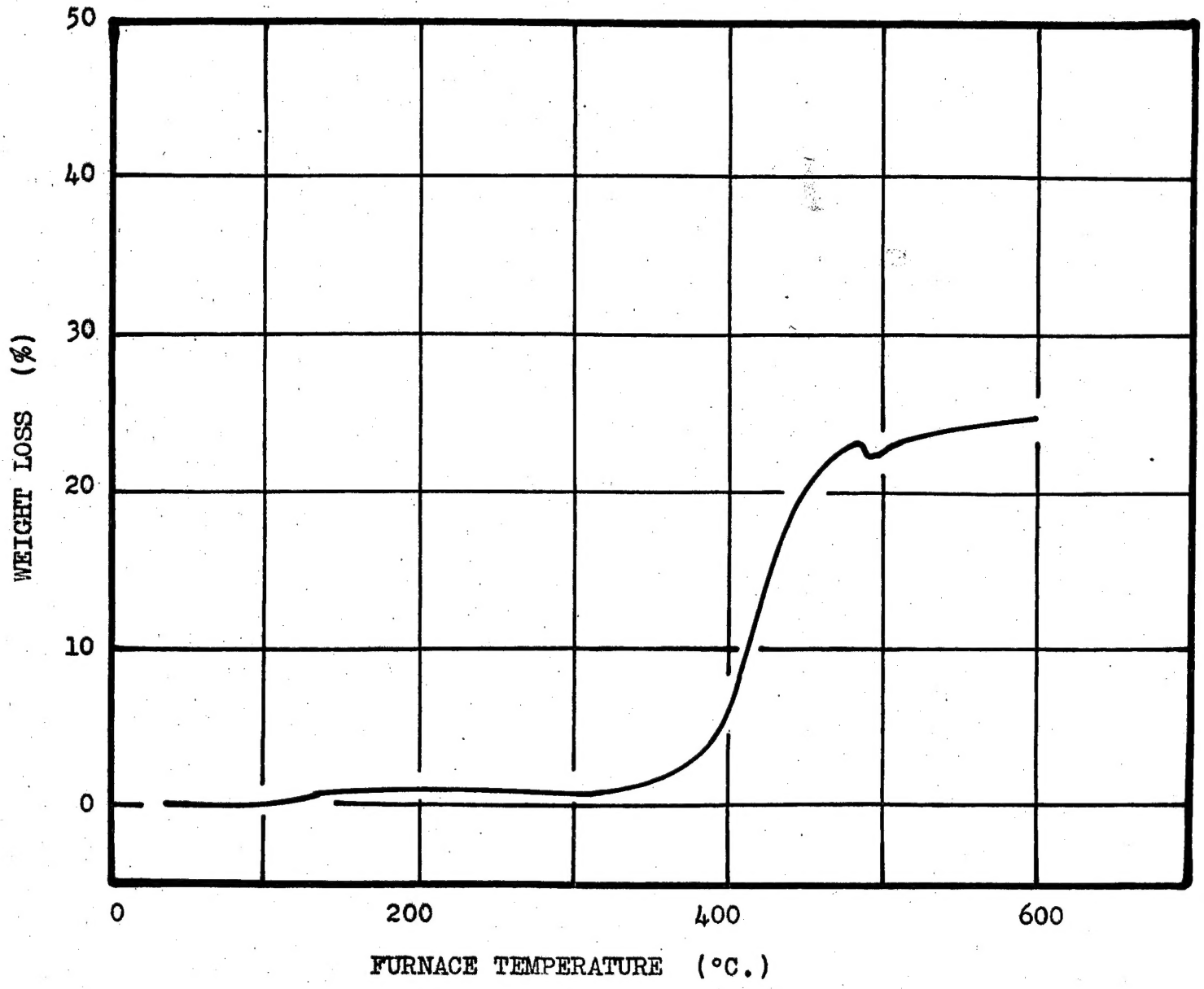


Fig. 1- TGA THERMOGRAM OF CARBORANE SILICONE ELASTOMER GUM

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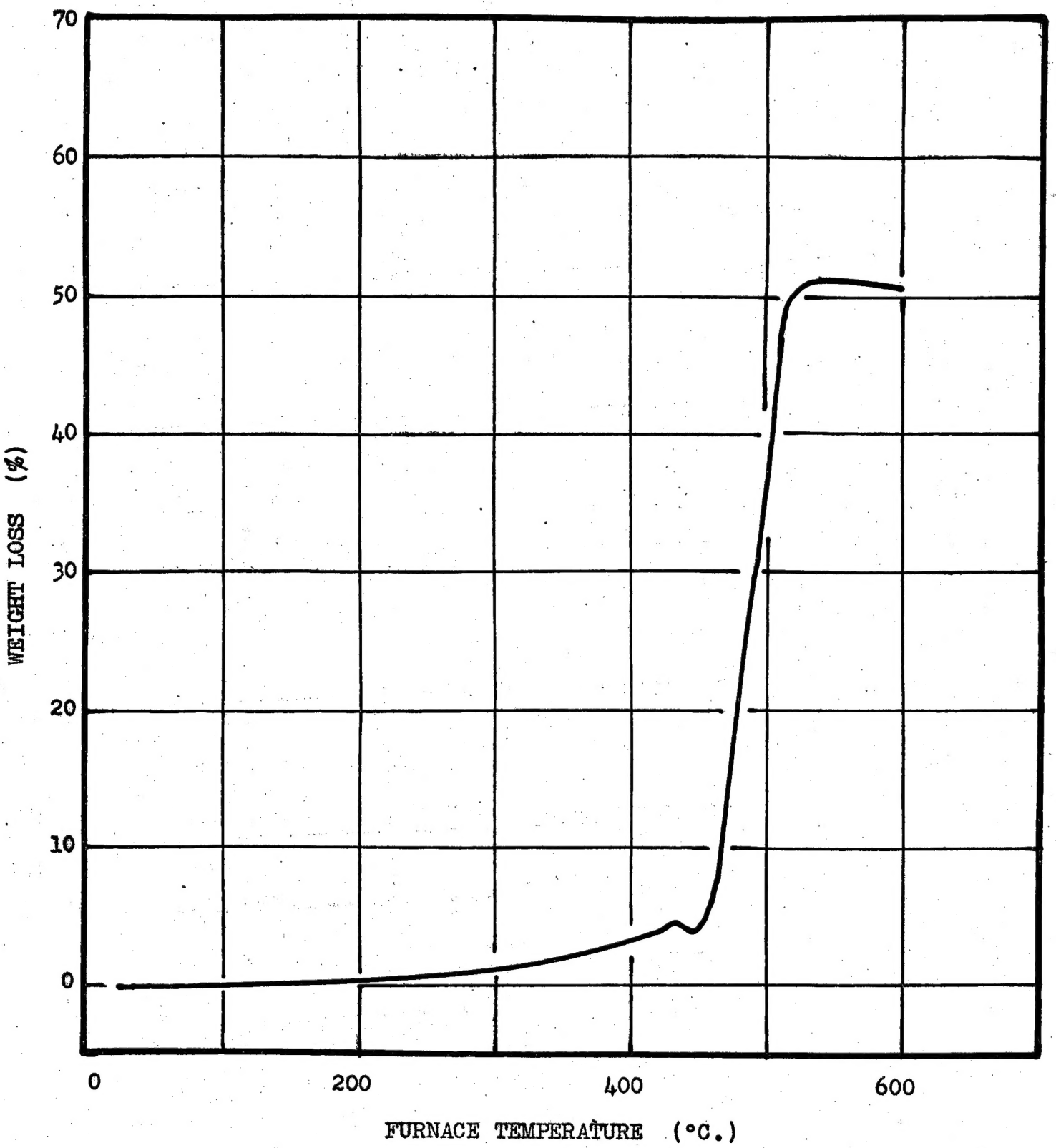

Fig. 2-TGA THERMOGRAM OF COPOLYMER E107-5309(RM)

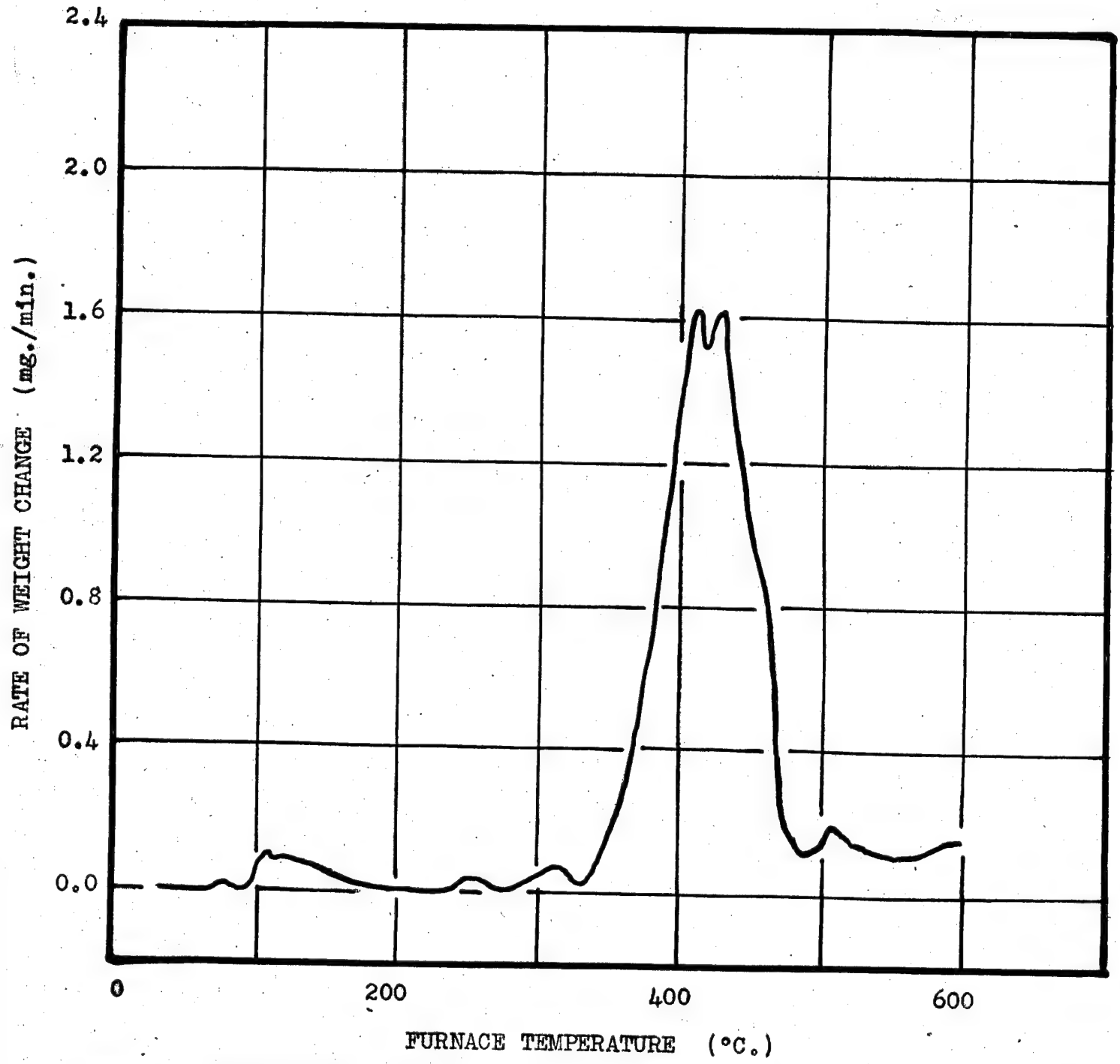

Fig. 3- DIFFERENTIAL TGA THERMOGRAM OF CARBORANE SILICONE ELASTOMER GUM

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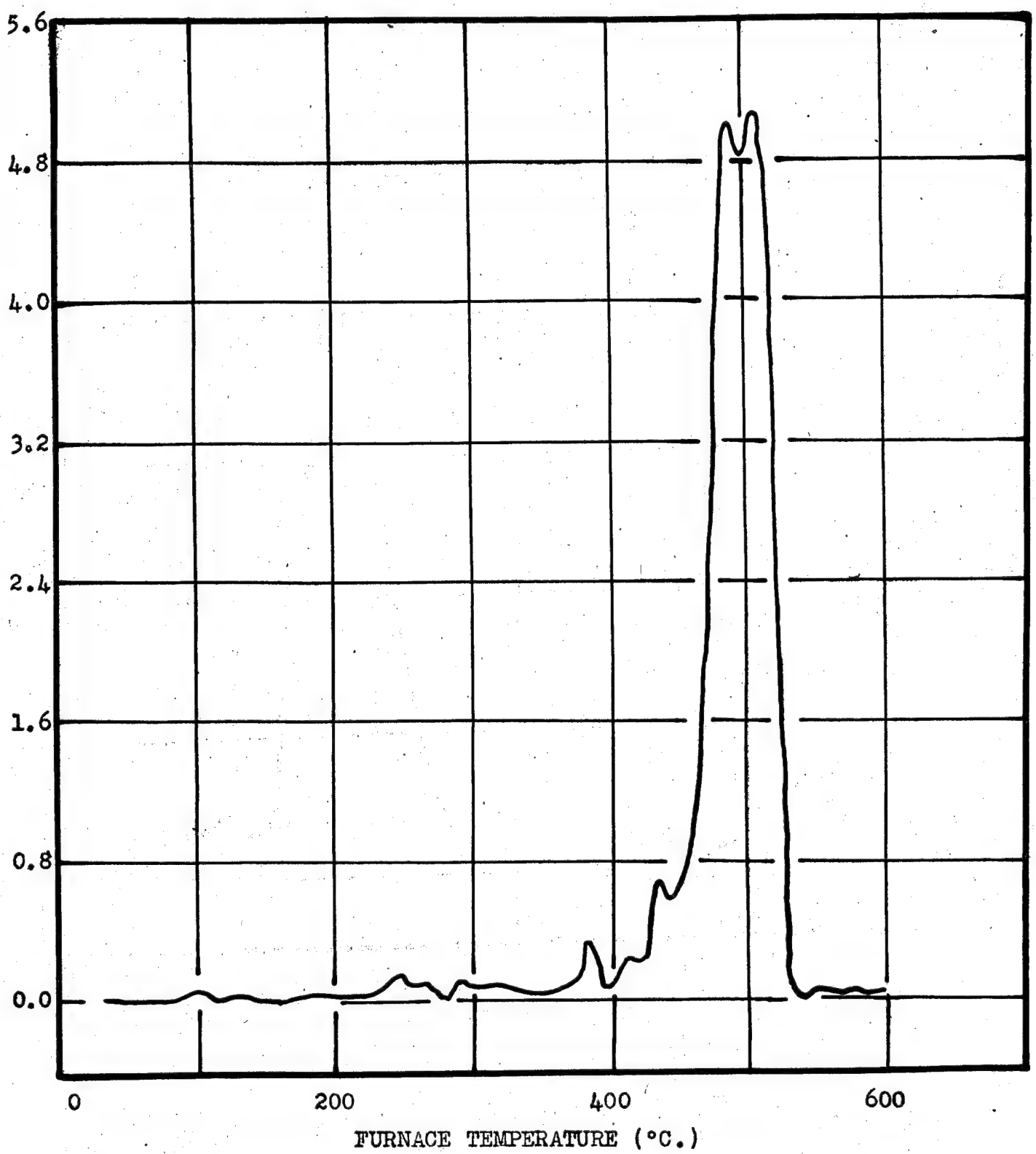

Fig. 4- DIFFERENTIAL TGA THERMOGRAM OF COPOLYMER E107-5309(RM)

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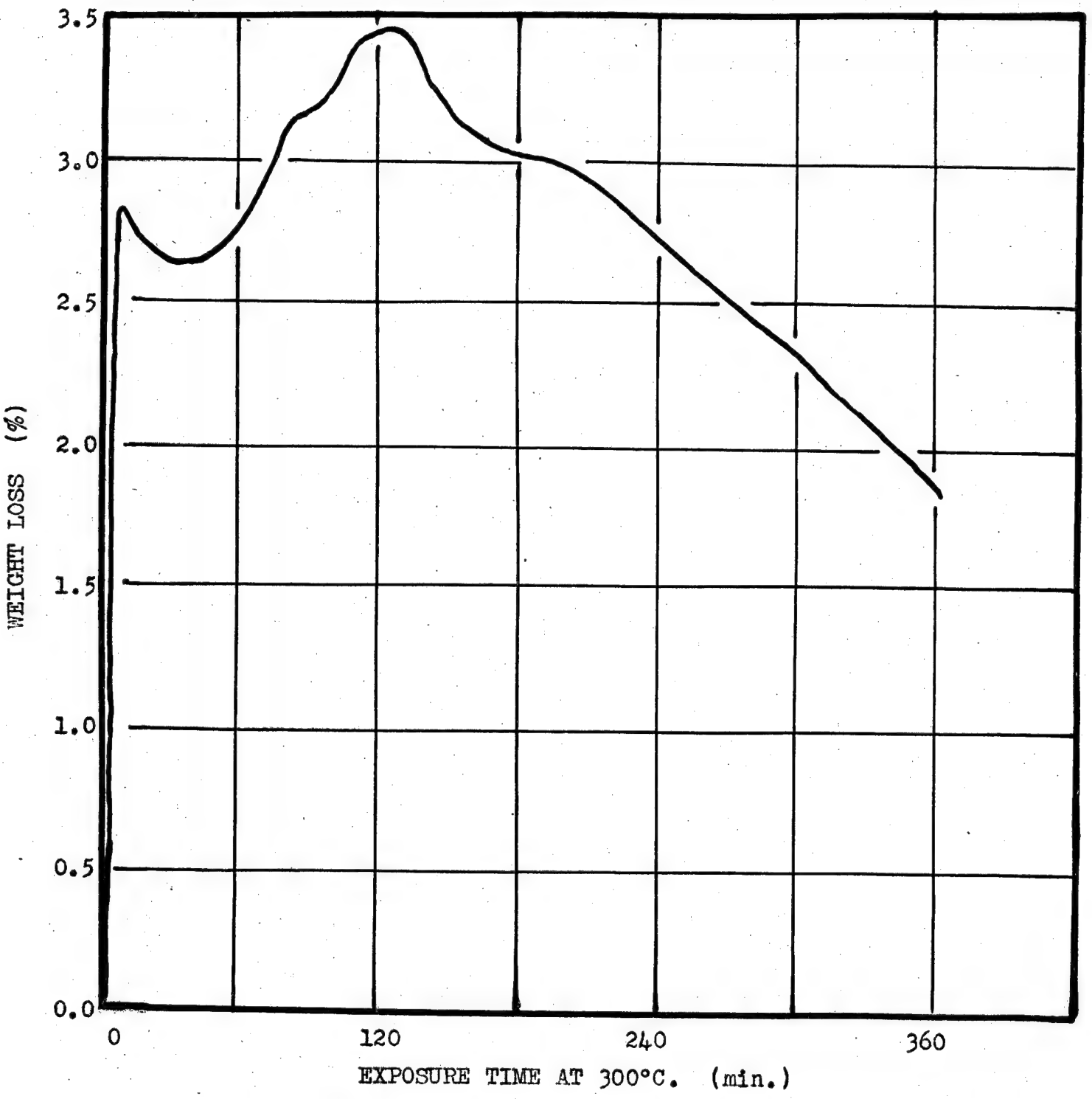

Fig. 5-ITGA THERMOGRAM OF CARBORANE SILICONE ELASTOMER GUM AT 300°C.

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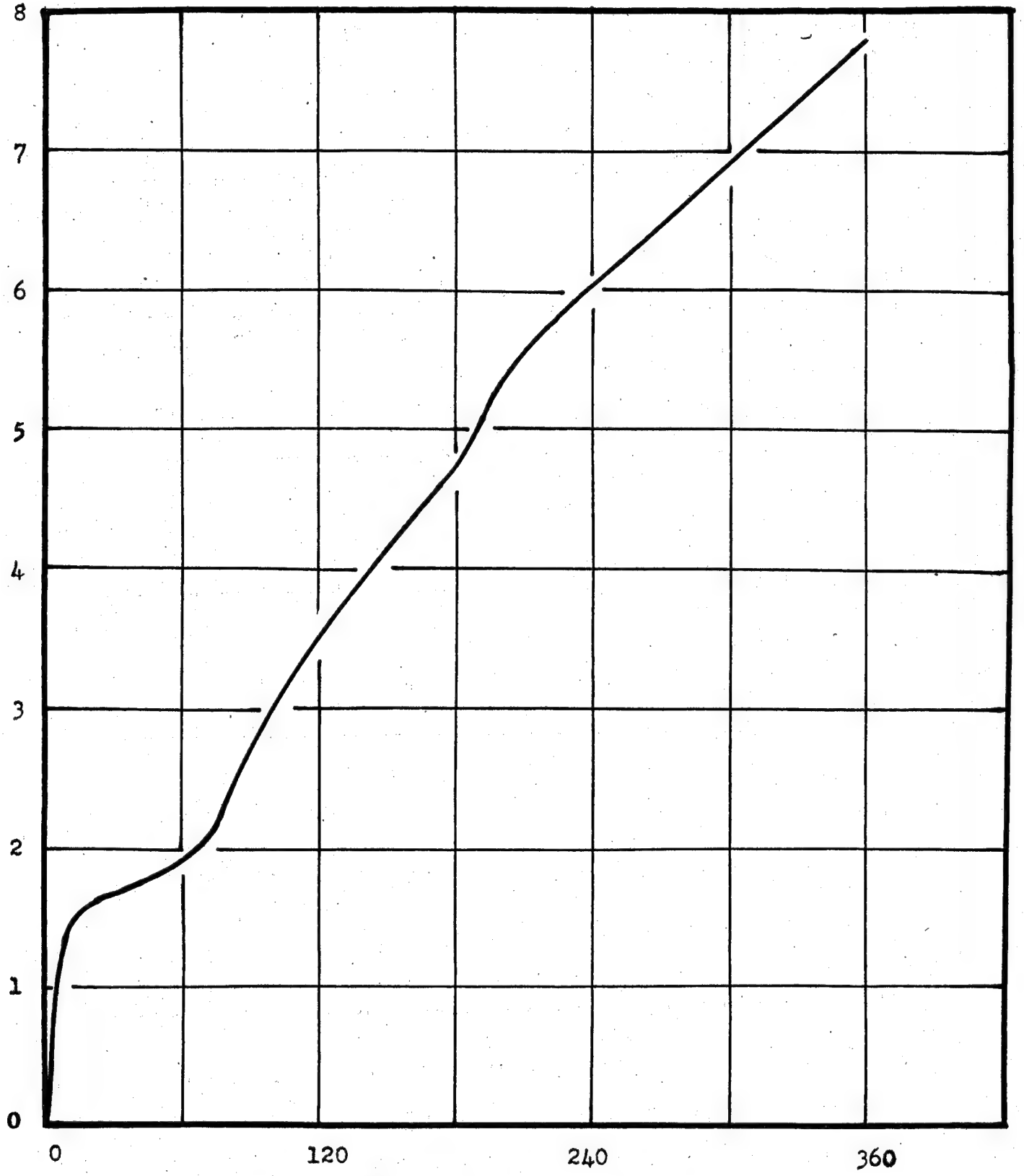

Fig. 6-ITGA THERMOGRAM OF COPOLYMER E107-5309(RM) AT 300°C.

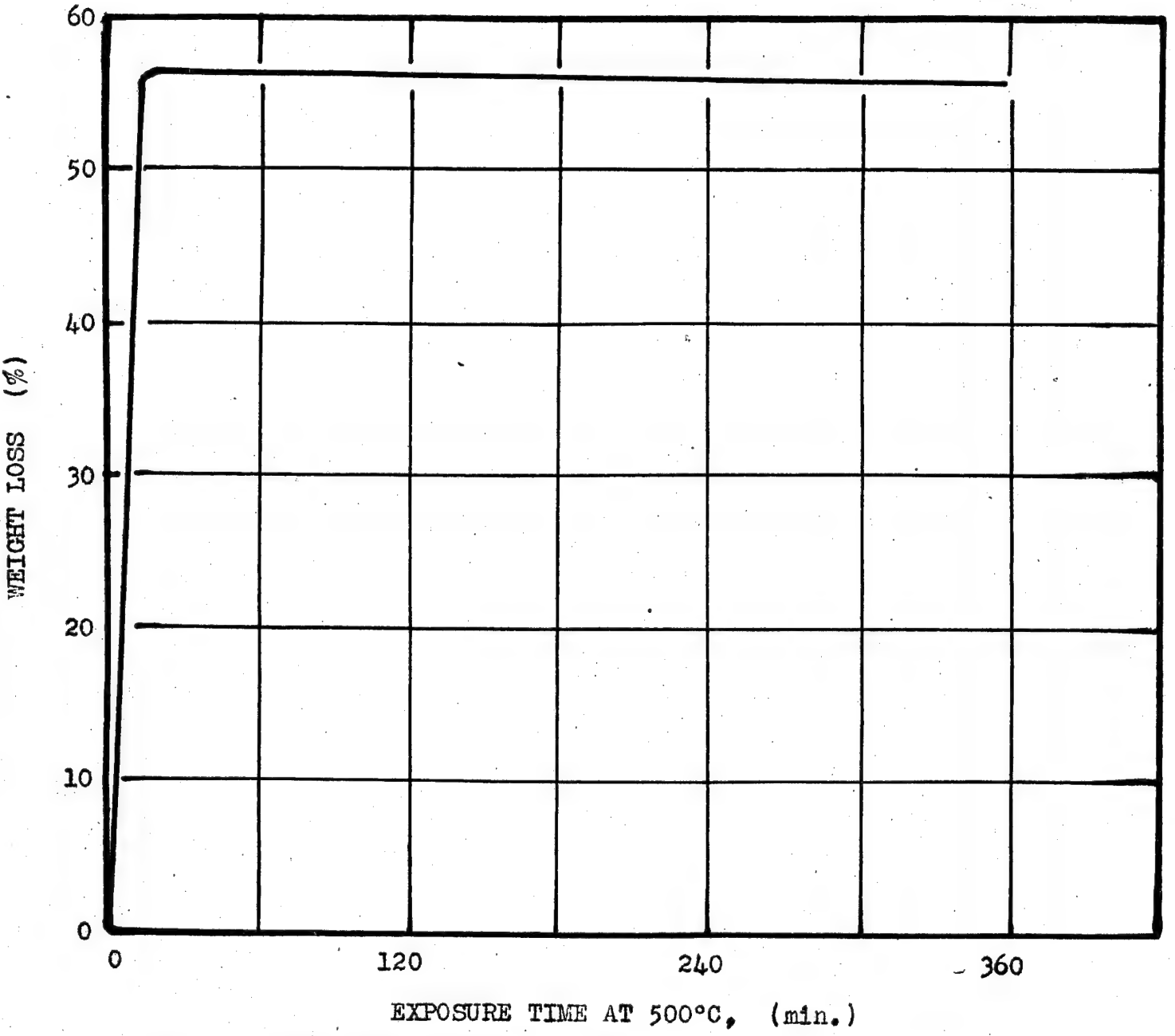

Fig. 7- ITGA THERMOGRAM OF CARBORANE SILICONE ELASTOMER GUM AT 500°C.

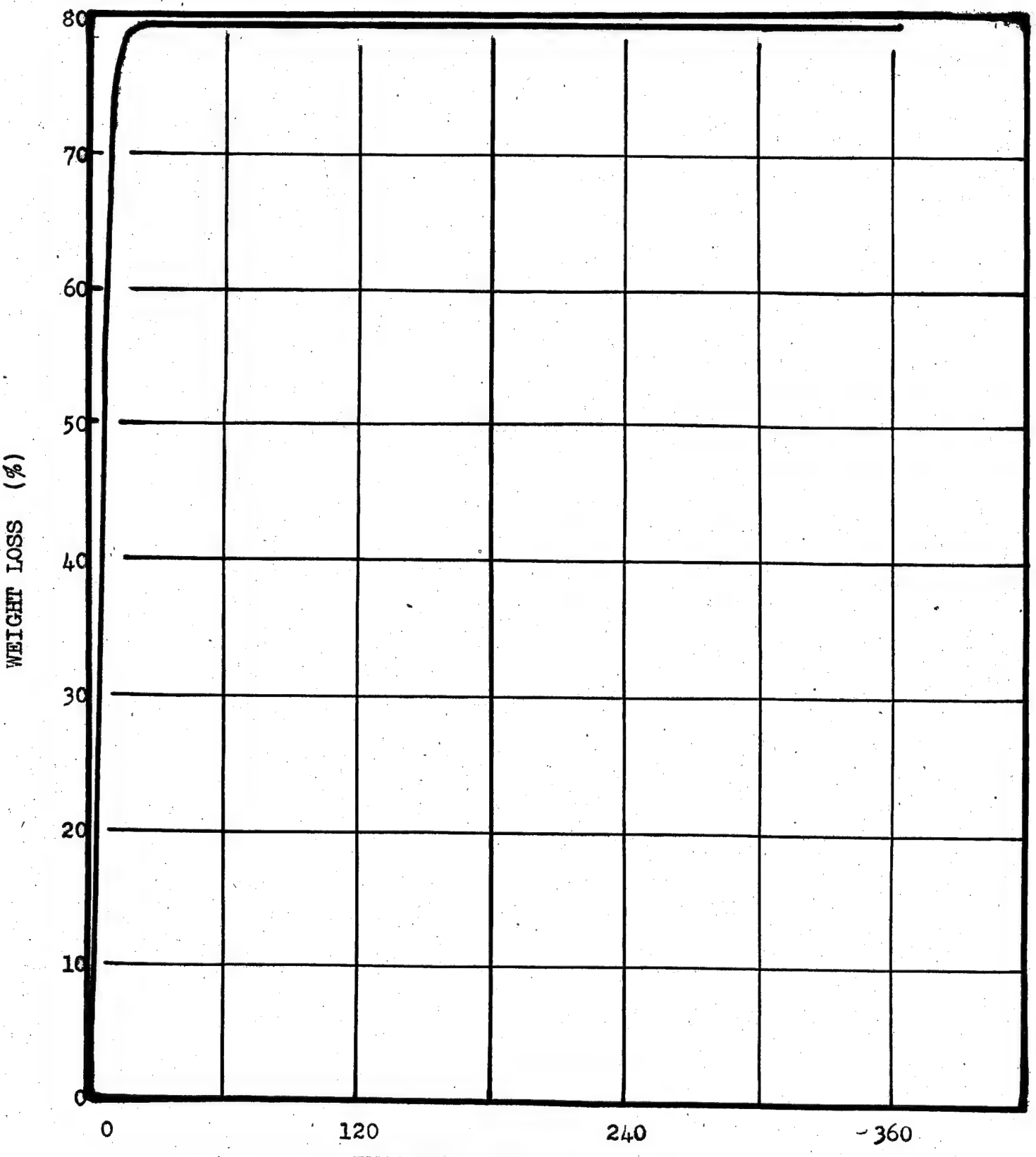

Fig. 8- ITGA THERMOGRAM OF COPOLYMER E107-5309(RM) AT 500°C.

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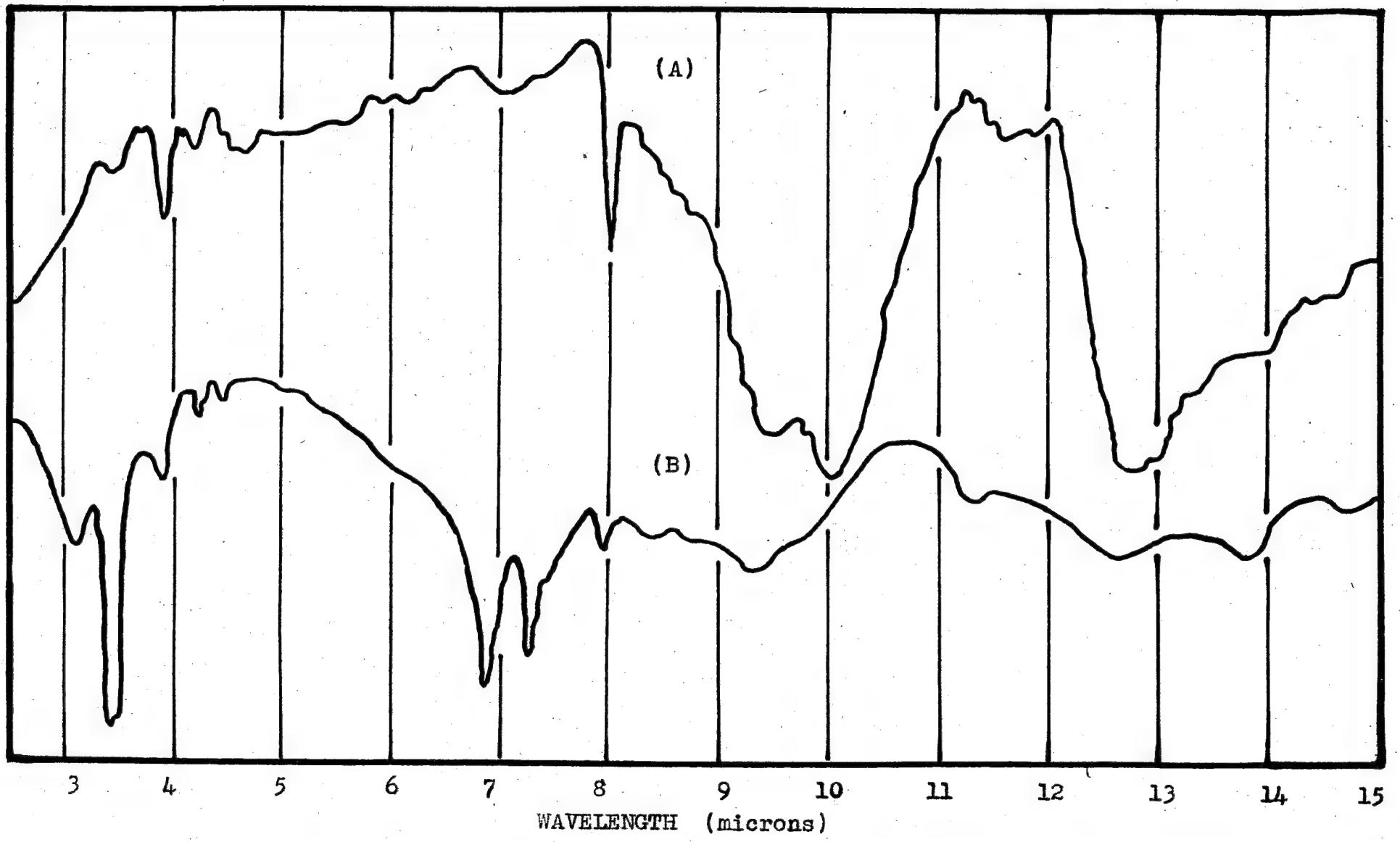

Fig. 9- INFRARED SPECTRA OF (A) UNTREATED CARBORANE SILICONE ELASTOMER GUM AND (B) ITGA RESIDUE AFTER 6 hrs. At 300°C.

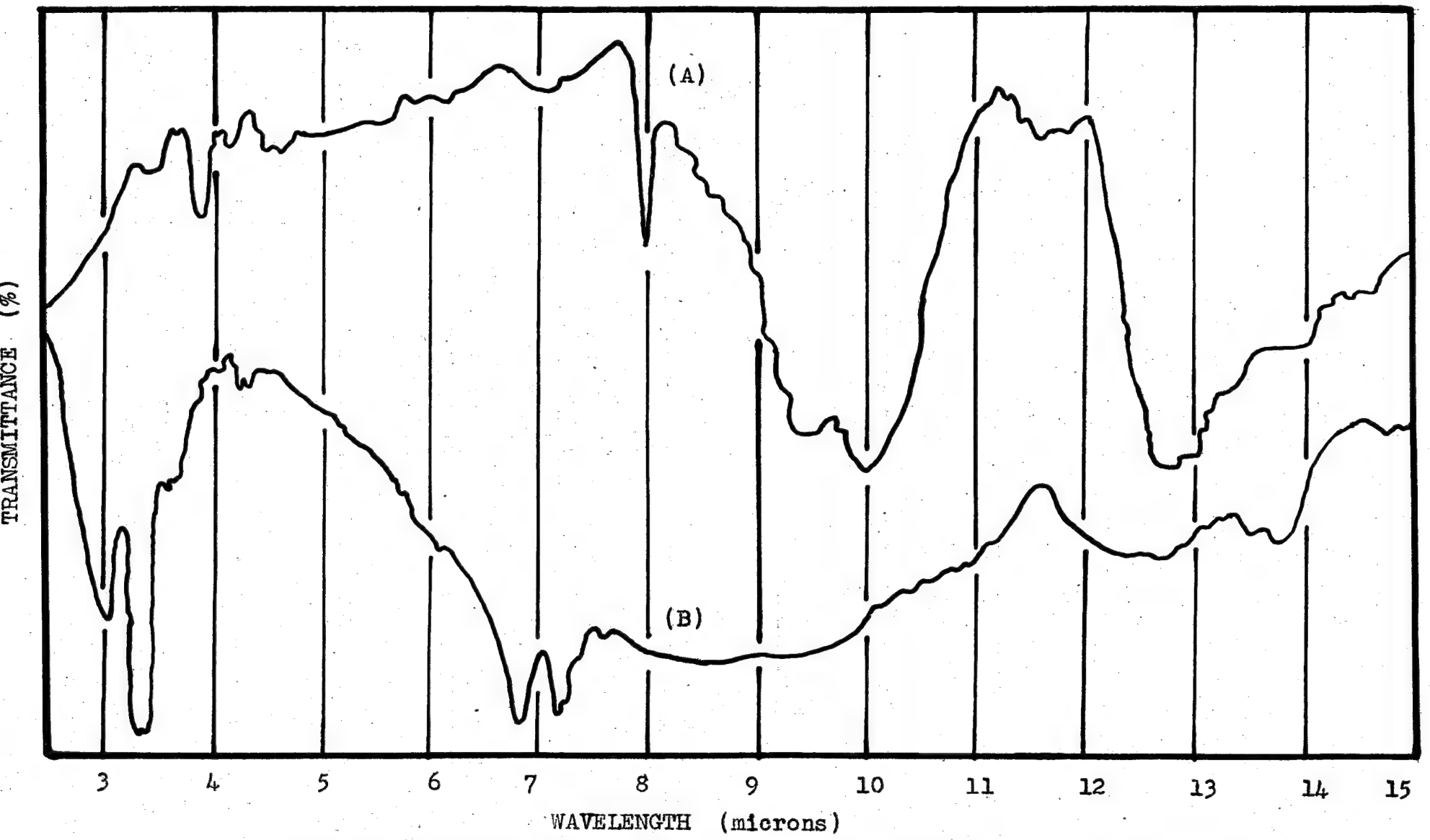

Fig. 10- INFRARED SPECTRA OF (A) UNTREATED CARBORANE SILICONE ELASTOMER GUM AND (B) ITGA RESIDUE AFTER 6 hrs. At 500°C.

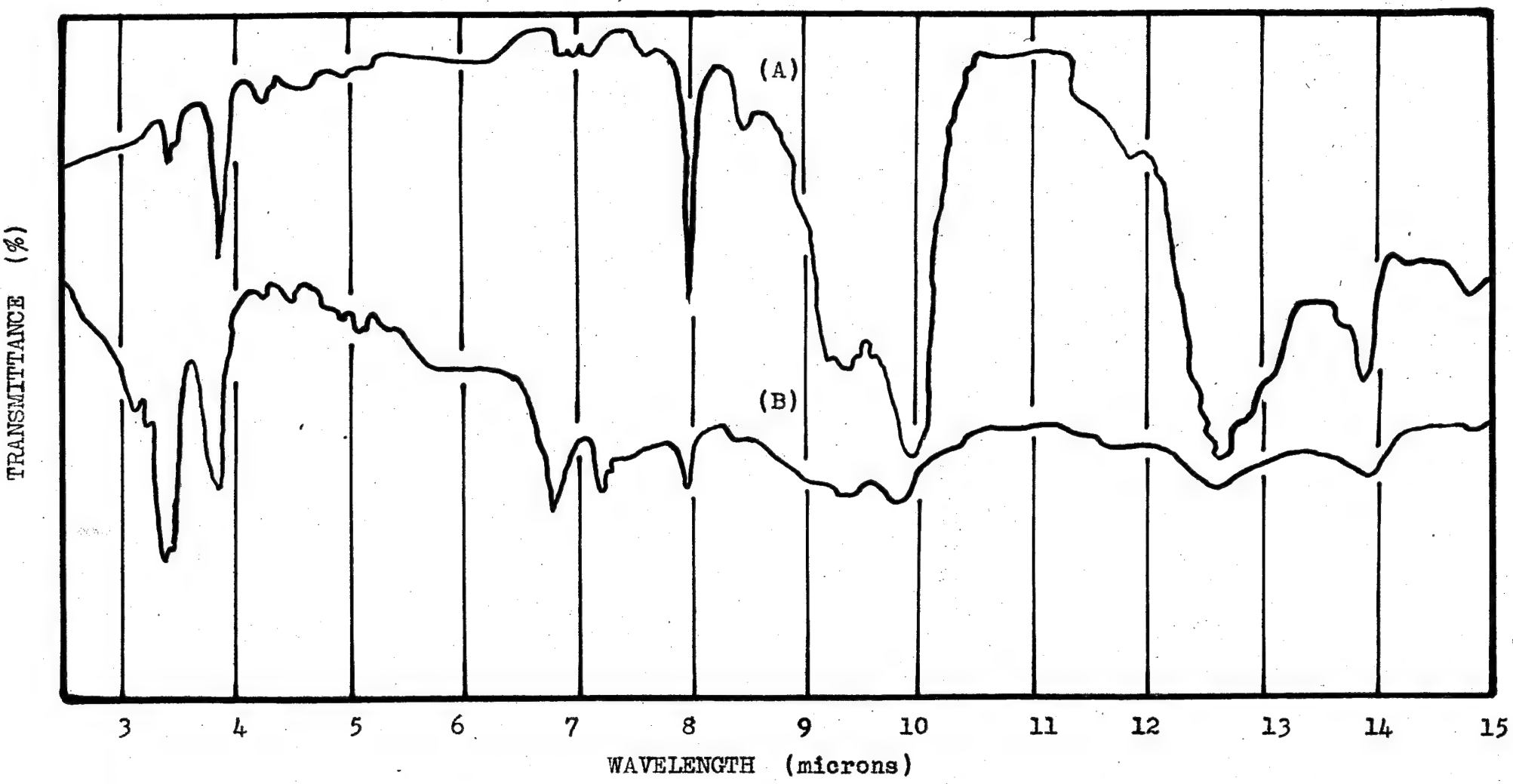

Fig. 11- INFRARED SPECTRA OF (A) UNTREATED COPOLYMER E107-5309(RM) AND (B) ITGA RESIDUE AFTER 6 hrs. At 300°C.

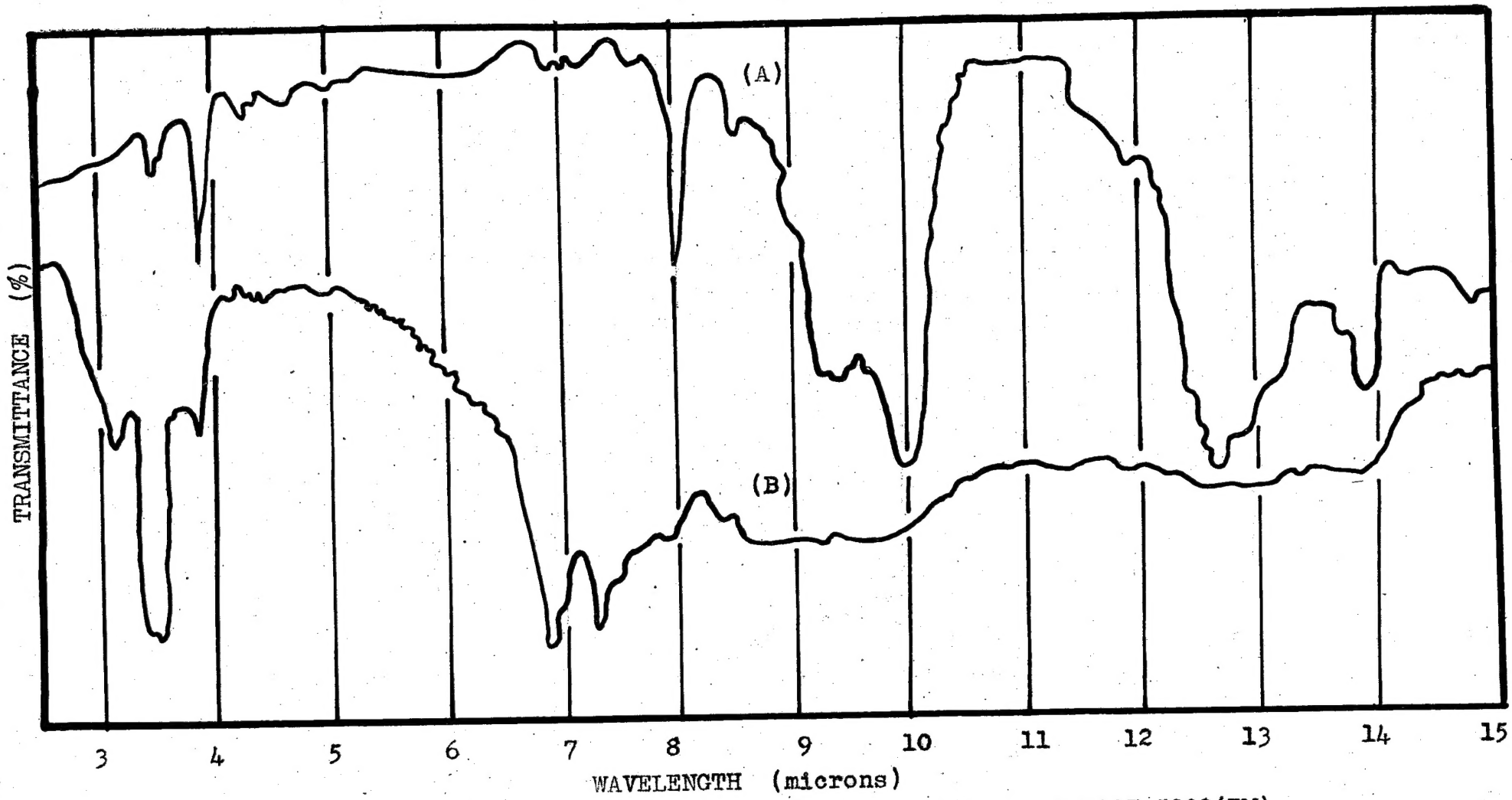

Fig. 12-INFRARED SPECTRA OF (A) UNTREATED COPOLYMER E107-5309(RM) AND (B) ITGA RESIDUE AFTER 6 hrs. At 500°C.

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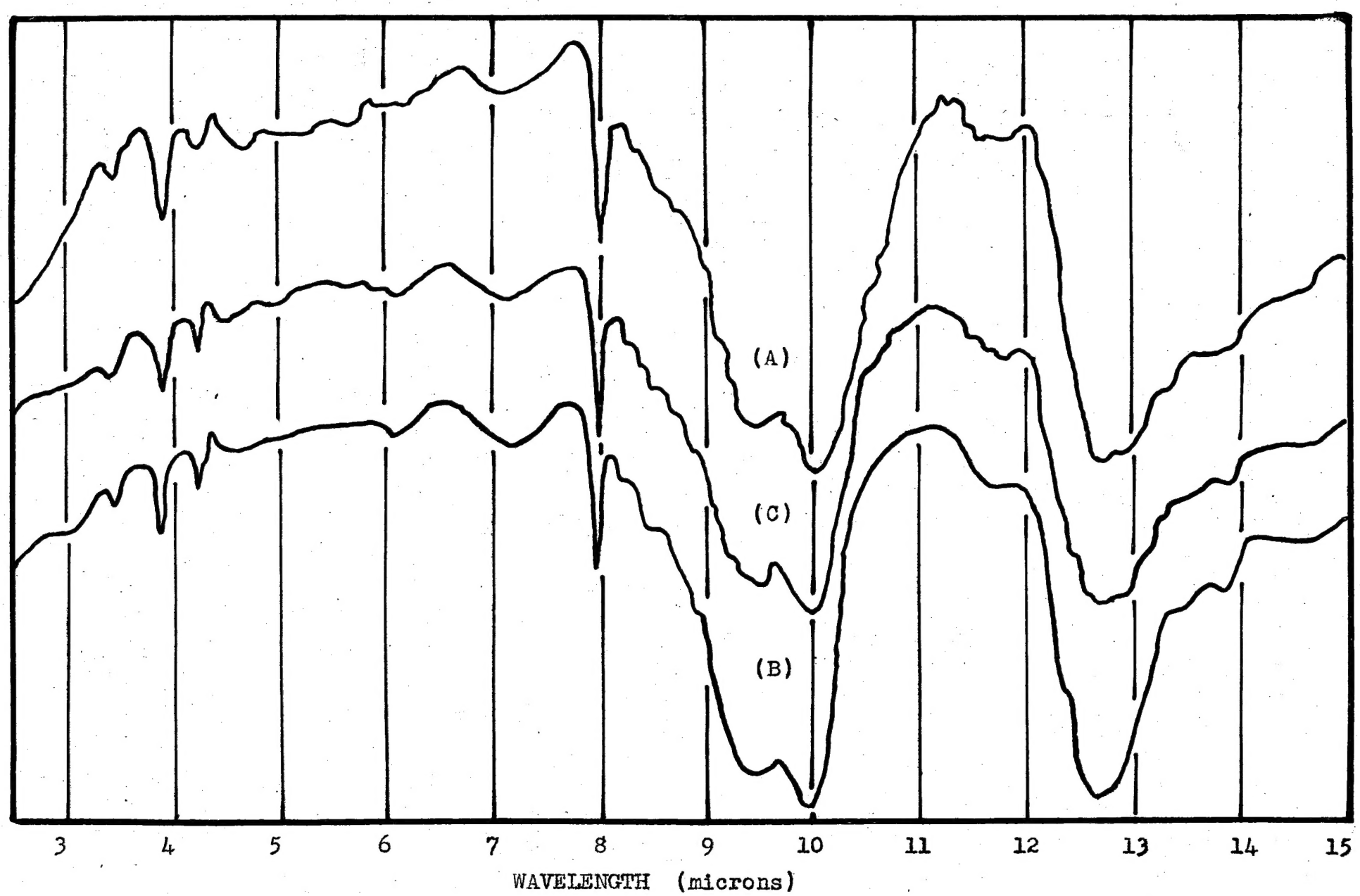

Fig. 13- INFRARED SPECTRA OF (A) UNTREATED CARBORANE SILICONE ELASTOMER GUM; (B) AFTER 4 hrs. In BOILING H_2O; AND (C) AFTER 24 hrs. in H_2O at ROOM TEMPERATURE

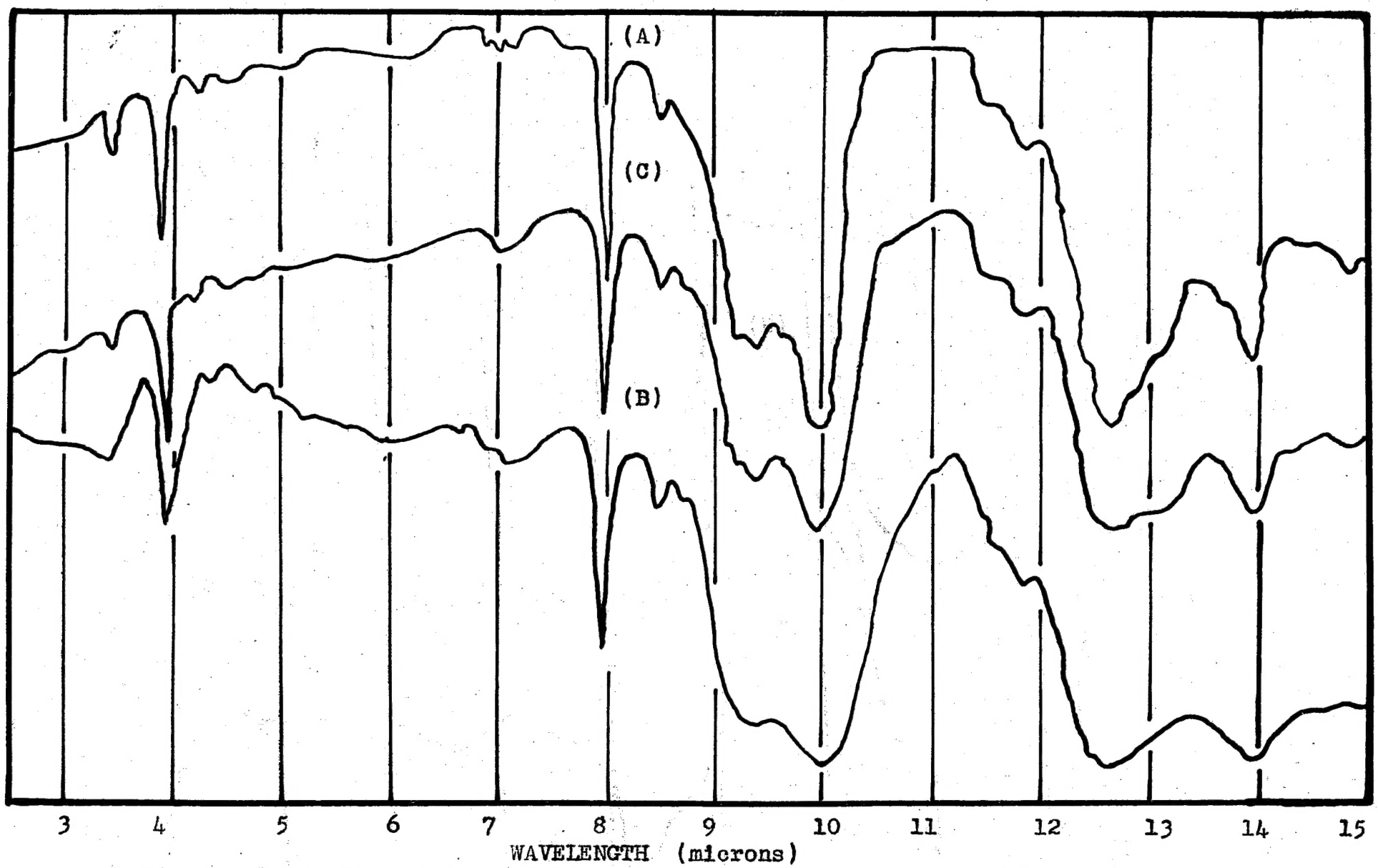

Fig. 14- INFRARED SPECTRA OF (A) UNTREATED COPOLYMER E107-5309(RM); (B) AFTER 4 hrs. IN BOILING H_2O; AND AFTER 24 hrs. IN H_2O AT ROOM TEMPERATURE

TABLE 1

RESULTS OF THERMOGRAVIMETRIC ANALYSIS (TGA)

POLYMER	WEIGHT LOSS (%)			
	300°C.	400°C	500°C.	600°C
Carborane Silicone Elastomer Gum	1.1	15.8	23.6	25.4
Carborane Silicone Copolymer E 107-5309 (RM)	1.5	3.2	37.2	55.7